WATER SIDE CORROSION IN BOILERS - TATA STEEL'S EXPERIENCES

N. KRISHNASWAMY AND P.S. BHATTACHARYA
Tata Steel, Jamshedpur - 831 001

Introduction

Captive power plants in an integrated steel Plant like Tata Steel have got two basic functions to perform, viz. meeting the essential power requirement and supplying the process steam. Process steam requirement gets the first priority and has to be met under all conditions. Even though the steel plant may have a tie-up with the utility for getting a certain contracted power supply, the captive power plants have to produce the base load-the sum of the most essential loads which cannot be shed-off from equipment and process safety point of view-after meeting process steam demand. Under the present scenario of economic liberalisation, the cost of operations has to be brought down and kept at the lowest levels dictated by market forces. The capitve power plants can meet all these objectives only if all the boilers are operated at a high efficiency, availability and reliability.

Corrosion and other related problems are of great concern to power plant operators. A proper understanding of these aspects will go a long way in achieving the performance levels expected from the boilers and the machines they serve. This paper attempts to throw some light on some of the important areas which a boiler engineer must know for getting a high level of performance from the boilers.

Iron Contamination In Boilers - The Sources, The Problem And Its Control

It is well known to all boiler operators that many problems in boilers are directly related to corrosion or deposition of both soluble and insoluble iron and considerable time, effort and money are spent in fighting the battle of iron. Hence a sound understanding of the nature and sources of iron and the methodology of preventing its deposition on heat transfer surfaces is essential for efficient and reliable boiler operation.

Sources of Iron

Iron compounds contaminate the boiler from installation. The mill scale on the plates and pipes, weld slag and splatter, etc., are the initial source of iron, and if not removed completely, it will start a cycle of iron fouling. Initial hydrostatic tests are often carried out using oxygen laden water which results in the formation of rust on the

boiler internal surfaces. Improper lay-up procedures followed during long lay-off of a boiler also bring in significant quantity of iron into the boiler. During normal operation, corrosion in pre-boiler, boiler and after-boiler systems produce oxides of iron in varying degrees depending upon the competency of operation. Although boiler manufacturers spell out procedures for boiler start-up and shutdown, these are not always followed exactly as given. Sudden thermal expansions and contractions fracture the protective magnetite film leading to further corrosion and generating more oxide.

Although excessive iron can cause many problems, the worst is the formation of a constantly growing insulating deposit on a boiler tube in high heat flux area. If allowed to continue, failure of the tube will result due to overheating.

It is often said that a boiler is merely a film of magnetite supported by structural steel. The ideal magnetite film is thin, adherent and of constant thickness and texture. It is this film that protects the boiler during operation from further corrosion. Deposits of iron can destroy this protective film.

Salts present in boiler water can concentrate beneath the iron deposit and this too can cause failure through many mechanisms such as caustic corrosion, low pH corrosion, hydrogen damage, etc.

Transported iron oxide can foul Ion Exchange resin beds but this contamination can be controlled with proper cleaning of the resin.

Controlling the Problem of Iron

With boiler systems demanding greater reliability and efficiency, iron contamination heads the list of operator's concerns. Good practices and proper treatment can bring it under control. Some of the practices, followed with benefit in Tata Steel to combat this problem, are :

1. Precommissioning chemical cleaning of pre-boiler, boiler and some of the after-boiler systems.

   For the intermediate pressure boilers that we have, this was not considered essential some fifteen years. back. But now, this is considered as an essential step in commissioning.

2. Proper commissioning to ensure clean passivated internal surfaces in the boiler.

3. Maintenance of make-up water quality stringently.

As our boilers have to supply a significant quantity of process steam to the steel plant, DM water make-up is of the order 40 to 45%. Compromise in quality of make-up can lead to very serious problems reducing availability of boilers and turbines which we can ill-afford.

4. Use of stainless steel lines to transfer DM water to deaerators.

5. Select deaerators of proven design and monitor performance constantly.

The performace of a deaerator is as good as its design and hence a lot of care has to be taken while selecting the design and make. Spray type deaerators give more reliable and better performacne than try type.

6. Chemical cleaning of operating boilers based on deposit density monitoring.

It is a good practice to take sample pieces of furnace tubes from high heat flux areas during annual turnarounds to monitor deposit density and chemical composition and plan chemical cleaning when density exceeds 40 mg/cm^2. With good operating practices, we find need to acid clean the boilers once in about twelve years.

7. A proper feed water conditioning program to control corrosion in pre-boiler, boiler and after-boiler systems and periodic audit of the same by an expert agency.

8. Proper storage of idle boilers using either wet or dry method.

In Tata Steel, we do not face this situation normally, as boilers, whenever they are available, are kept in operation to meet power and process steam requirements.

Boiler Corrosion

To maintain reliable boiler operation, corrosion of boiler metal by the water used to generate steam must be prevented. Dissolved oxygen, high temperatures, and acid and caustic in the water can, if uncontrolled, severely pit, gouge or embrittle boiler tube metal and eventually lead to tube failure. It is necessary to understand the types of corrosion that can occur, their causes and - more importantly - their prevention.

Corrosion Essential to boiler operation

Since no oxygen is normally present, the primary corrosion reaction in an operating boiler is :

$$3\,Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

Iron — Water or steam — Magnetitie — Hydrogen Gas

The product of this process is black iron oxide or magnetitie that builds a tenacious layer at the steel surface. When the magnetite layer grows to a thickness of 0.0002 in. to 0.0007 in., damaging corrosion stops. Under changing temperatures and dynamic boiling environment, some damage takes place to this protective layer which is again restored. The normal corrosion progresses slowly at approximately 1 mil. (0.001 in) per year. The primary objective of boiler water treatment is to promote conditions that preserve the magnetite layer.

Types of Corrosion

1. Caustic Corrosion

The stability of magnetite layer is highly dependent on the pH of the boiler water. Fig. 1 shows the effect of pH on boiler corrosion or more accurately, magnetite dissolution. It is dissolved by both low pH and high pH environments.

The terms 'Caustic Gouging' and 'Ductile Gouging' refer to the corrosion under the action of localised concentrated sodium hydroxide. It is commonly encountered in :

* Water-cooled tubes in regions of high heat flux.
* Slanted or horizontal tubes.
* Locations beneath heavy deposits.
* Heat transfer regions at or adjacent to backing rings at welds or to other devices that disrupt flow.

Two critical factors that contribute to caustic corrosion are availability of sodium hydroxide or of alkaline-producing salts and the mechanism for concentration.

Some of the Mechanisms of concentration are

* *Departure from nucleate boiling (DNB) :* Under DNB condition, a stable film or blanket of steam forms on the tube surface. Corrosives concentrate at the edges of this blanket.
* Under-deposit concentration. Fig. 2 explains the mechanism of under-deposit concentration.
* *Evaporation at a water line :* When a waterline exists, corrosives may concentrate by evaporation resulting in gouging along the waterline.
* *Indications of caustic corrosion :* Hemispherical or elliptical depressions, filled with corrosion products and sometimes containing sparkling crystals of magnetite. At times, there may be a crust of hard deposits and corrosion products containing magnetite crystals. The affected metal surface generally has a smooth, rolling contour.

Elimination

* Reduce the amount of available free NaOH.
* Prevent inadvertent release of caustic regeneration chemicals from DM Plant.
* Prevent in-leakages of alkaline-producing salts into condensers.
* Prevent DNB
* Prevent excessive waterside deposition

* Prevent the creation of waterlines in tubes

* Prevent process contamination.

2. *Low pH Corrosion*

A general depression of bulk-water pH may, although very rare, occur if certain acidic contaminants enter the boiler. The more common low-pH attack arises due to localised conditions. Two circumstances must exist simultaneously to produce this condition :

* Availability of acid producing salts or free acid. Acid producing salts may find way through condenser leakage. Unitentional additions of free acid may arise from inadvertent release of acid regeneration chemicals into DM water make-up.

* Mechanism of concentration: This is same as in caustic corrosion.

To eliminate low pH attack, the above two conditions must be tackled. It is very difficult to distinguish low-pH attack and caustic corrosion as in the locations where they are found and in visual appearance they are the same. However, metallographic examination will distinguish the two.

3. *Low-pH Corrosion During Acid Cleaning*

If propere procedures are not followed during acid cleaning, corrosion of internal surfaces of a boiler will result from low-pH exposure. Thermally induced breakdown of inhibitor, inappropriate selection of cleaning agent or its strength, excessive exposure times, excessive exposure temperatures, failure to completely neutralise, etc. are some of the factors that lead to uncontrolled acid corrosion.

One of the first areas to be affected is the tube ends inside the mud and steam drums. Hand-hole covers, drum manholes, and shell welds may also be affected. Heat transfer surfaces and weldments may experience vigorous attack. Shielded regions within crevices and under remaining deposits may prevent proper neutralisation of cleaning acid. This results in vigorous localised attacks when the boiler is returned to service.

4. *Hydrogen Damage*

Hydrogen demage may occur where corrosion reactions result in the production of atomic hydrogen. Damage may result from high-pH or low pH corrosion reactions. Atomic hydrogen liberated diffuses into the steel. Some of this diffused atomic hydrogen will combine at the grain boundaries or inclusions in the metal to produce molecular hydrogen or will react with iron carbides in the metal to produce methane. These gases accumulate at the grain boundaries producing discontinuous integranular micro cracks. When such micro cracks accumulate, a part

of the wall of the tube bursts giving rise to a thick-walled failure.

Generally, hydrogen damage is confined to water-cooled tubes in boilers operating above 1000 psi. Steps to eliminate caustic corrosion and low-pH attack will eliminate the possibility of hydrogen damage.

5. *Oxygen Corrosion*

Oxygen corrosion is a complex electrochemical reaction that results in pitting in a small area of the metal surface. If uncontrolled, it finally leads to pin-hole type of failures of tubes. Oxygen corrosion sites present knoblike mounds of corrosion products that frequently cover pits. These mounds are known as tubercles which indicate presence of oxygen corrosion.

The three critical factors for the onset and progress of oxygen corrosion are presence of moisture of water, presence of dissolved oxygen and an unprotected metal surface.

Corrosiveness of water increases as temperatue and dissolved solids increase and as pH decreases. Aggressiveness increases with an increase in oxygen.

An unprotected metal surface can be present under the following conditions :

* The metal surface is bare, e.g., the surface after acid cleaning without passivation.
* The metal surface is covered with a marginally protective or non-protective iron oxide such as hematite.
* Cracks exist in the protective Magnetite film. Crack occur due to mechanical and thermal stresses during normal boiler operation, start-up, shut down and rapid load swings. When proper operating conditions are maintained, the cracks get repaired and magnetite film reforms. However, if excessive levels of oxygen are present, the cracks cannot be adequately repaired and corrosion commences.

Locations of Oxygen Corrosion : In an operating boiler, the first areas to be affected are the economiser and feed water heaters. In cases of severe oxygen contamination, other areas such as waterline in the steam drum and steam separation equipment are corroded.

Oxygen attack is more of a problem in idle boilers. The entire boiler system is susceptible but the most common attack sites are the bends in superheater tubes where moisture can collect.

Control in Operating Boiler: This is effected by bringing down dissolved oxygen to very low levels.

To achieve this dissolved oxygen level, an excess of chemical deaerant is needed in the boiler water. Recommended residuals are 20 to 60 ppm of sulphite or 0.1 to 0.5

ppm of hydrazine, depending upon the scavenger used. Daily tests will show the level of excess. Records should be kept of the amount of chemical deaerant fed. This record provides a constant efficiency check of mechanical deaeration as well as indication of any infiltration of dissolved oxygen into the system.

Possible causes of excessive levels of dissolved oxygen are improper functioning of deaerator, improper feed of oxygen scavenging chemicals and air in-leakage. Monitoring of oxygen levels at the economiser inlet, especially during start up and low load operation, is recommended. Elimination of oxygen corrosion in an operating boiler is achieved by looking at these aspects very carefully and taking remedial actions. The results that can be achieved could be surprising in some cases. Table No. 1 indicates how economiser leakages due to oxygen corrosion could be brought under control in two boilers of same operating life with the above mentioned approach and in one case, costly replacement of complete economiser could be avoided with no difference in reliability.

Control in Idle Boiler : An idle boiler will have to be protected by using proper procedure of wet lay-up or dry lay-up if oxygen corrosion is to be avoided. The wet lay-up procedure involves complete filling of the boiler with water of very low oxygen content, use of sufficiently high levels of oxygen scavenging chemicals, maintenance of properly adjusted pH levels and periodic water circulation. Successful protection of an idle boiler during dry lay-up depends upon consistent elimination of moisture and/or oxygen involving use of dessicants and nitrogen blanket or continuous circulation of dry, dehumidified air (<30% RH).

Protection of a Boiler After Acid Cleaning: This is achieved by developing a protective magnetite film coating on the metal surfae through rinsing followed by a post boiloutpassivating step.

6. Corrosion due to Copper

Pitting of boiler drums and tube banks has been encountered due to metallic copper deposits formed during acid cleaning procedures which do not completely compensate for the amount of copper oxides in the original deposits. Dissolved copper may be plated out on freshly cleaned steel surfaces, eventally establishing anodic corrosion areas and forming pits very similar to oxygen in form and appearance. In most cases, it is localised in certain tube banks, giving rise to random pitting in those particular areas. Whenever deposits are formed containing large quantities of copper oxide or metallic copper, special precautions are required to prevent plating out of copper during cleaning operations.

7. Corrosion Fatigue Cracking

Corrosion fatigue failures most frequently occur in boilers that are in "peaking" service. used discontinuously or otherwise operated cyclically. Rapid start-up or shutdown

can greatly increase the possibility of corrosion fatigue.

Corrosion fatigue refers to cracks propagating through a metal as a result of cyclic tensile stresses operating in an environment that is corrosive to the metal. Two common sources of cyclic tensile stresses are cyclically fluctuating internal pressure and constrained thermal expansion and contraction. Operation at low-pH levels or with excessively high levels of dissolved oxygen may induce pitting. The pits act as stress concentrators for the initiation of corrosion-fatigue cracks.

The sequence of crack development is :

* *During first phase of cyclic stress, the tube wall undergoes expansion when the oxide layer which is brittle may fracture.*

* *The exposed metal surface at the root of the crack oxidesess forming a microscopic notch in the metal surface.*

* *During the expansion cycle, the oxide layer will tend to fracture along this notch, causing it to deepen.*

* *As this cyclic process continues, a wedge shaped crack propagates through the tube wall until rupture occurs.*

The cracks always propagate in a direction perpendicular to the direction of the principal stress. They are typically straight and unbranched, are needle or wedge-shaped and propagate perfpendicular to the metal surface. They often occur in families of parallel cracks.

Reduction or elimination of corrosion-fatigue cracking is achieved by controlling cyclic tensile stresses, controlling environmental factors and boiler design.

Conclusion

Of all the problems in boiler operation, corrosion and corrosion-related problems are, by far, the most serious. If they are allowed to continue unchecked, the direct and indirect monetary loss to the organisation on account of them can be very substantial. However, if proper care is taken during commisioning and subsequent operation of the boiler, corrosion and its effects can be kept at a low level and a long, efficient and trouble-free life of the boiler and all associated equipment can be ensured.

Table - 1

Economiser leakage due to oxygen corrosion in Boilers No. 1 & 2 at Power House No. 4

Year of Commisioning : Boiler No. 1 1973
Boiler No. 2 1974

No. of oxygen corrosion leaks

Year	Boiler No. 1	Boiler No. 2	Remarks
1974	1	-	
1975	-	-	
1976	-	-	
1977	-	2	
1978	-	-	
1979	2	2	
1980	1	1	
1981	4	-	Economiser sections coompletely replaced in Boiler No. 1 only in 1981. Modifications to deaerators and other operational controls to reduce dissolved oxygen introuduced in both boilers in 1981 and 1982. Decided not to replace economiser sections in Boiler No. 2
1982	-	-	
1983	-	-	
1984	1	-	
1985	1	-	
1986	-	-	
1987	-	-	
1988	-	1	
1989	-	1	
1990	-	-	
1991	-	-	
1992	-	-	
1993	1	2	
1994	-	-	

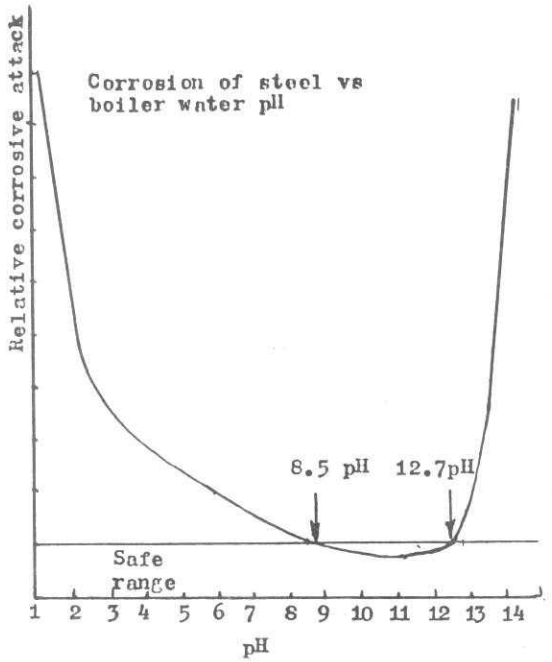
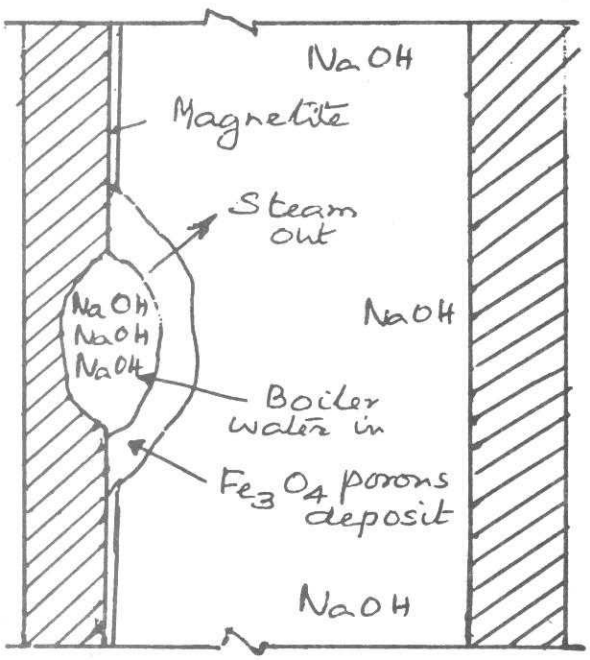


Fig. 1 High or low pH boiler water conditions corrode boiler steel



1 Liter 5ppm NaOH
5 grams NaOH x 1000 ml Soln.
10^6 gram Solution
= 0.005 grams NaOH
Concentrating Mechanism at the Tube Wall
0.1 ml solution containing
0.005 grams NaOH

<u>0.005 grams NaOH</u>
0.1 ml Solution
= 50,000 ppm

Fig. 2 Concentration of caustic can occur beneath deposition